



Short communication

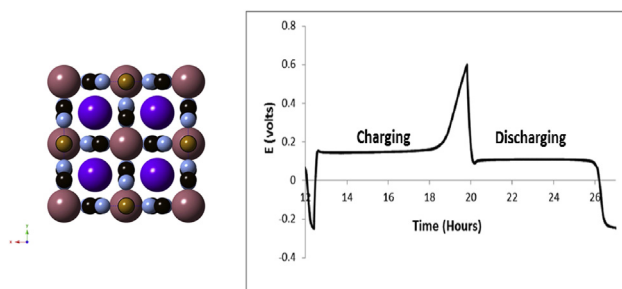
Potassium barium hexacyanoferrate – A potential cathode material for rechargeable calcium ion batteries

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HIGHLIGHTS

- $K_2BaFe(CN)_6$ has been demonstrated as a battery cathode for the first time.
- Demonstrated divalent Ca^{2+} ion battery action in mixed solvent system.
- Demonstrated reversible capacity of $55.8 \text{ mA hr g}^{-1}$ and coulombic efficiency of 93.8%.
- Studied the effect of water on the cathode material using EIS.

GRAPHICAL ABSTRACT



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ABSTRACT

Potassium barium hexacyanoferrate ($K_2BaFe(CN)_6$) was investigated as a cathode material for reversible Ca^{2+} ion insertion/extraction type rechargeable battery using non-aqueous electrolytes. The electrochemical performance of $K_2BaFe(CN)_6$ was evaluated using cyclic voltammetry and galvanic cycling at ambient temperature. It is shown that addition of water led to significant enhancement in intercalation and de-intercalation of Ca^{2+} ions, leading to improved charge/discharge capacity. The enhancement in performance is attributed to formation of solvation spheres around the intercalating Ca^{2+} ions which provide screening from the electrostatic charges of the $BaFe(CN)_6$ lattice. A reversible capacity of $55.8 \text{ mA hr g}^{-1}$ and a coulombic efficiency of 93.8% was demonstrated at the end of 30 charge/discharge cycles.

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1. Introduction

The proliferation of portable electronic devices and the appeal of electrical vehicles have highlighted the need for high energy

density electrochemically rechargeable batteries. Currently, the highest energy density rechargeable commercial battery technology available is based on the monovalent Li ion. In principle, if the monovalent cations can be replaced by multivalent cations, then this can lead to high volumetric energy density batteries. The multivalent cations that have been examined to achieve this include Mg^{+2} [1–6,19], Ca^{+2} [5,7–10,19], Ba^{+2} [19], Sr^{+2} [19], Zn^{+2} [11], Al^{+3} [11], Y^{+3} [5], and Cu^{+2} [12]. Besides the potential of delivering high capacity batteries, an attractive feature of many of these metals includes lower cost as compared to that of Li.

When selecting an intercalating cation for batteries, one of the factors considered is the ionic radius. Mg has been relatively

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thoroughly investigated since its ionic radius of 72 pm [13] is small and close that of Li ions. However, the standard electrode potential (SEP) of Mg is somewhat low (−2.36 V vs. NHE). On the other hand, Ca^{2+} ion has a relatively large ionic radius of 118 pm, but also has a larger SEP (−2.87 V vs. NHE), comparable to that of lithium. When solvation spheres are taken into account, doubly charged ions have an even larger radius. In aqueous environments the hydrated radii of Li^+ , K^+ , Mg^{2+} and Ca^{2+} are 382 pm, 331 pm, 428 pm, and 412 pm, respectively [21]. The large ionic radius of Ca^{2+} (especially solvated Ca^{2+}) would necessitate a lattice with larger d-spacing for reversible intercalation.

One of the major obstacles to realization of rechargeable multivalent batteries has been a lack of an appropriate intercalation cathode material. Vanadium oxides have been investigated as cathode materials for several multivalent cations [3,5,6,8,9], as have molybdenum and titanium sulfides and selenides [4,10]. In this investigation we have examined hexacyanoferrate lattices as cathode material for Ca^{2+} intercalation batteries. Hexacyanoferrates have a cubic lattice with relatively large d-spacing. The d-spacing can be further expanded by incorporating larger ions such as Ba^{2+} in the lattice framework. Although, barium dust in its elemental and oxide form are known to cause skin and eye irritation, barium in a compound form such as potassium barium hexacyanoferrate ($\text{K}_2\text{BaFe}(\text{CN})_6$) is less toxic. However, alternate approaches, such as replacing barium with more benign, larger radii and lighter elements such as strontium, would help alleviate toxicity concerns.

Besides the size of many of the multiply ionized species, one of the major issues is that the multiply ionized cations result in high polarization strength that induces strong electronic interaction with the host material lattice, resulting in poor intercalation and/or diffusion of the cations. One way to overcome this hurdle is by introducing a small quantity of water to the organic electrolyte so that the hydration sphere formed around these multivalent cations shield them from the strong coulombic interactions with the ions of the host material, hence reducing the barrier to intercalation [5,14]. We present below our initial results of a Ca^{2+} ion battery where the cathode material is potassium barium hexacyanoferrate. It is shown that addition of a small quantity of water significantly improves its performance.

2. Experimental section

2.1. Synthesis

Potassium barium hexacyanoferrate ($\text{K}_2\text{BaFe}(\text{CN})_6$) was synthesized by employing a room temperature wet chemical precipitation technique. Equimolar concentrations of barium nitrate ($\text{Ba}(\text{NO}_3)_2$) and potassium ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6$) solutions (10 mmol in 15 ml deionized (di) water) were mixed together at room temperature. Barium nitrate solution was slowly dropped into the potassium ferrocyanide solution using a pipette. In about 30 s, crystals of potassium barium hexacyanoferrate ($\text{K}_2\text{BaFe}(\text{CN})_6$) precipitated out of the solution. The crystals were repeatedly cleaned (five times) using di water with the aid of centrifugation at about 7000 rpm for 5 min. The crystals were then dried at room temperature under ambient conditions.

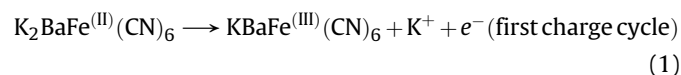
2.2. Characterization

The phase composition of the $\text{K}_2\text{BaFe}(\text{CN})_6$ sample was characterized using powder X-ray diffractometry (PXRD). Data was collected in a focused beam (Bragg–Brentano) geometry on a Rigaku Model Ultima IV X-ray diffraction system using graphite-monochromatized $\text{CuK}\alpha$ radiation. Scans were performed over an angular range of 10° – 80° 2θ at room temperature. Cyclic voltammetry and galvanic cycling were performed with an EG&G 273 A

potentiostat. Nyquist plots were recorded using the EG&G 273 A potentiostat and a Solartron 1260 impedance metre.

2.3. Electrochemistry set-up

The electrochemical performance of $\text{K}_2\text{BaFe}(\text{CN})_6$ was evaluated using cyclic voltammetry and galvanic cycling at ambient temperature. The test cell was comprised of a glass container with three electrodes, where a graphite rod acted as a counter electrode, carbon paper coated with $\text{K}_2\text{BaFe}(\text{CN})_6$ was the working electrode, and Ag/AgCl (saturated KCl) filled capillary was the reference electrode. All the measurements were made with 1 cm^2 of the working electrode exposed to the electrolyte solution. The stock electrolyte for all measurements was composed of 1 M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile as the organic solvent. Initial measurements were performed using the stock electrolyte. Subsequently, a specific amount of water was added to the electrolyte solution as described below. The cathode composite electrode was prepared by mixing $\text{K}_2\text{BaFe}(\text{CN})_6$ powder with multi-walled carbon nanotubes, carbon black and polyvinylidene fluoride (PVDF) binder in a ratio of 80:9:2:9 and finely ground using a mortar and pestle. A slurry was prepared by adding a few drops of N-methyl-2-pyrrolidone (NMP) to above formed homogeneous powder and spread on both sides of a carbon paper which acted as the current collector. The positive electrode material loading was about 4.25 mg cm^{-2} . The slurry coated electrodes were initially dried at room temperature and further dried under vacuum at 100°C for 1 h. In the present work, charging is represented by de-calciation and discharging by calciation of the $\text{K}_2\text{BaFe}(\text{CN})_6$ electrode, which is used as a cathode as indicated by the following reaction mechanism:



Equation (1) represents the reaction of the first charge cycle and Equation (2) the reaction for the subsequent discharge and charge cycles. For charge–discharge measurements, the electrodes were subjected to a C-rate of C/7 with an upper cut-off voltage of 0.5 V and a lower cut-off voltage of -0.25 V with reference to Ag/AgCl (saturated KCl).

3. Results and discussion

The x-ray diffraction spectrum of the dried $\text{K}_2\text{BaFe}(\text{CN})_6$ powder is shown in Fig. 1. The dominant peaks occur at 16.10° , 32.50° and 49.50° . It is evident from the width of the peaks that the as formed $\text{K}_2\text{BaFe}(\text{CN})_6$ possessed good crystallinity. $\text{K}_2\text{BaFe}(\text{CN})_6$ has been synthesized previously [20], where the lattice parameters were determined to be $a_0 = b_0 = 10.148 \text{ \AA}$ and $c_0 = 10.981 \text{ \AA}$. A unit cell for these parameters is shown in Fig. 2. It was recently predicted that doubly charged intercalated ions are not present at the BCC locations within the lattice, but at the FCC locations [22].

The cyclic voltammetry response is shown in Fig. 3a for $\text{K}_2\text{BaFe}(\text{CN})_6$ as the positive electrode in 35 ml of the acetonitrile/ $\text{Ca}(\text{ClO}_4)_2$ anhydrous stock solution, and with 3 ml (8%) DI water in the stock solution, measured at a scan rate of 0.5 mV s^{-1} . The response does not show the presence of any redox peaks which indicates a lack of intercalation of Ca^{2+} ions into the lattice of $\text{K}_2\text{BaFe}(\text{CN})_6$. However, upon the addition of 6 ml (17%) di water to the 1 M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile stock electrolyte solution, sharp oxidation and reduction peaks are observed at 0.28 V and 0.11 V,

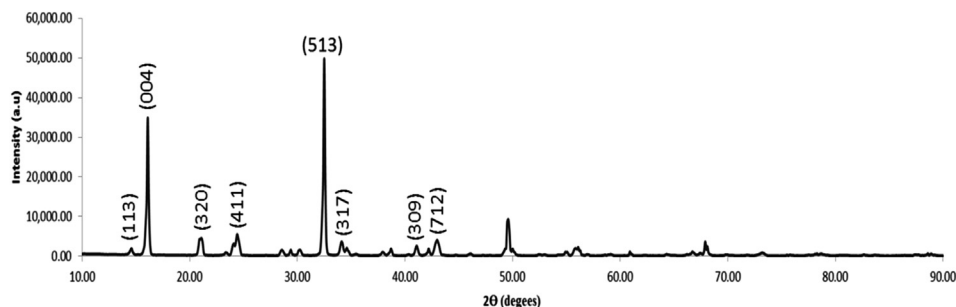


Fig. 1. Powder XRD pattern of the as synthesized $K_2BaFe(CN)_6$.

indicative of reversible removal and insertion of Ca^{2+} ions, respectively, into the bulk lattice of $K_2BaFe(CN)_6$ crystals. This response is shown on a larger scale in Fig. 3a. For reference, cyclic voltammetry of the $K_2BaFe(CN)_6$ cathode in 1 M aqueous solution of $Ca(NO_3)_2$ is shown in Fig. 3b.

Galvanic charge–discharge cycling of the $K_2BaFe(CN)_6$ positive electrode with 1 M $Ca(ClO_4)_2$ in acetonitrile are carried out at a current density of 12.5 mA g^{-1} , resulting in a discharge capacity of 7.6 mA hr g^{-1} . The response lacks flat charge and discharge plateaus, indicative of absence of solid state diffusion of the intercalating Ca^{2+} cations into the host lattice, but the sloped profiles are indicative of an electrical double layer based capacitor. However, upon adding 17% di water to the electrolyte solution, there is a significant presence of the charge and discharge plateaus at 0.148 V and 0.104 V, respectively, as shown in Fig. 4. A single plateau during discharging implies a one step insertion reaction. The variation in specific capacity and the columbic efficiency of the cathode electrode over 30 charge–discharge cycles is shown in Fig. 5. Both the charge and discharge capacities increased gradually over the first twelve cycles, finally, settling down by the fourteenth cycle, which has been observed before and attributed to stabilization of the cathode material [23,24]. The cathode demonstrated a columbic efficiency of around 93.8% with a charge capacity of $62.2 \text{ mA hr g}^{-1}$ and a discharge capacity of $55.8 \text{ mA hr g}^{-1}$ at the end of 30 cycles, leading to a reversible specific capacity of $55.8 \text{ mA hr g}^{-1}$ at the end of 30 cycles, which is about 80% of the estimated theoretical capacity of 70 mA hr g^{-1} for $K_2BaFe(CN)_6$. The theoretical capacities of Prussian blue analogues can vary with the amount of zeolitic water present in the lattice and are difficult to compute due to the varying

concentrations of water in the lattice of these materials, which is a function temperature and humidity.

A fundamental step in the charge/discharge process is the charge transfer at the electrode–electrolyte interface. This can be modelled by an equivalent circuit considering the ions at the electrode–electrolyte interface as adsorbed intermediates [15]. Then, the interfacial charge transfer resistance can be considered as the insertion resistance of the adsorbed ions into the host matrix [16]. To measure the charge transfer resistance, electrochemical impedance spectroscopy (EIS) measurements are carried out. Before the EIS measurements are performed, the cell is held at a constant potential of 0.05 V for 1 h in order to achieve equilibrium at the electrode–electrolyte interface representing the dc bias used in the EIS measurements. The dc bias is determined from the cyclic voltammetry and is selected such that the current at the selected dc potential is minimal.

Nyquist plots for potassium barium hexacyanoferrate in the stock electrolyte solution and subsequent additions of 8% and 17% DI water to the electrolyte solution, are shown in Fig. 6. The charge transfer resistance is computed by least square fit of the Nyquist plots to a Randles-type equivalent circuit [17,18]. The charge transfer resistance is determined to be 0.77Ω for 1 M calcium perchlorate in acetonitrile only electrolyte, 0.65Ω for 1 M calcium perchlorate in acetonitrile with 8% of di water, and 0.639Ω for 1 M calcium perchlorate in acetonitrile with 17% di water. The linear decrease (over the range examined) in the charge transfer resistance at the electrode interface upon addition of di water implies lowering of a resistance barrier for the intercalation of the Ca^{2+} ions from the bulk electrolyte into the barium hexacyanoferrate compound.

Enhancement of insertion of mono- and multi-valent ions into host matrices in the presence of water molecules in an organic electrolyte has been reported previously and has been attributed to strong solvation effects [3,18,14]. Water molecule assisted insertion of monovalent ions has been reported in Prussian blue [14], whereas the multivalent ions have been mostly intercalated into vanadium oxide based hosts [6]. We believe that a similar mechanism is responsible in our case. Our voltammetry and galvanic charge/discharge cycling data shows that without any water or with only 8% water, there is none to minimal redox activity implying that the Ca^{2+} ions are not inserted into the $K_2BaFe(CN)_6$ lattice. However, with 17% water, both cyclic voltammetry and galvanic cycling response are significantly enhanced. We attribute this change to the decrease in the size of the sheath around the calcium ions in the electrolyte upon addition of 17% water, leading to the diffusion of the Ca^{2+} ions into the host lattice sites. Apparently, a critical number of water molecules are required for the formation of a favourable solvation sphere around the cations. Our EIS data indicates lowering of the resistance for insertion of the ions into the host lattice with the addition of water. We also believe that

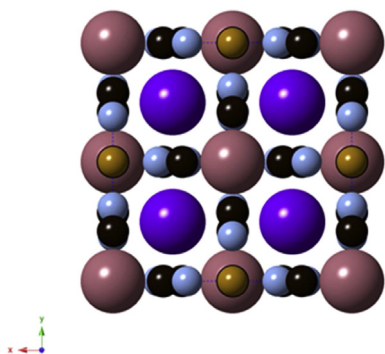


Fig. 2. Crystal structure of $K_2BaFe(CN)_6$ with the Ba^{2+} ions represented by spheres in red, Fe^{2+} ions represented by spheres in light brown, the CN^- presented by the light blue and black spheres and the K^+ ions in the interstitial sites are presented by violet spheres. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

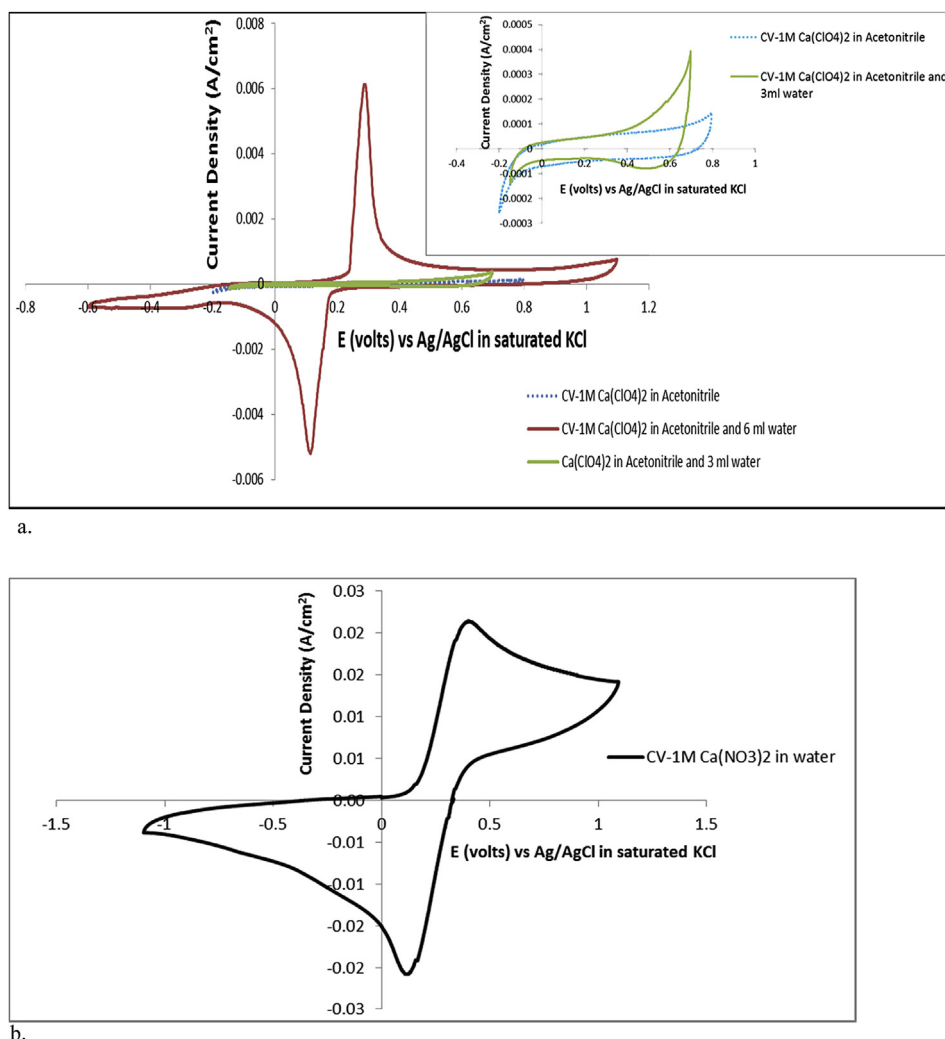


Fig. 3. a. Cyclic voltammetry of the $\text{K}_2\text{BaFe}(\text{CN})_6$ cathode in stock solution (dashed line) and with 3 ml of water (solid line) is shown in the inset. Large redox peaks are observed upon adding 6 ml water (red solid line). All scans were performed at 0.5 mV s^{-1} . b. Cyclic voltammetry of the $\text{K}_2\text{BaFe}(\text{CN})_6$ cathode in 1 M aqueous solution of $\text{Ca}(\text{NO}_3)_2$. The scan was performed at 25 mV s^{-1} . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the presence of water in the electrolyte leads to the hydration of the host lattice [20], further leading to the shielding of the strong coulombic interactions between the high charge density of the Ca^{2+} ions and the electron rich nitrogen present in the CN^- anion that makes up the barium hexacyanoferrate lattice. This shielding would allow the Ca^{2+} ions to diffuse in and out of the host lattice during discharge and charge cycles, with relatively small electrostatic perturbations, resulting in very flat charging and discharging

plateaus. We should note that further increase in composition of water leads slowly to dissolution of the $\text{K}_2\text{BaFe}(\text{CN})_6$ cathode. Strong redox activity is also observed in an aqueous electrolyte as shown in Fig. 3b, but the system is unstable due to dissolution of the active electrode material. Similar experiments with addition of water to propylene carbonate as the solvent did not produce significant enhancement in intercalation, indicating influence of the solvent.

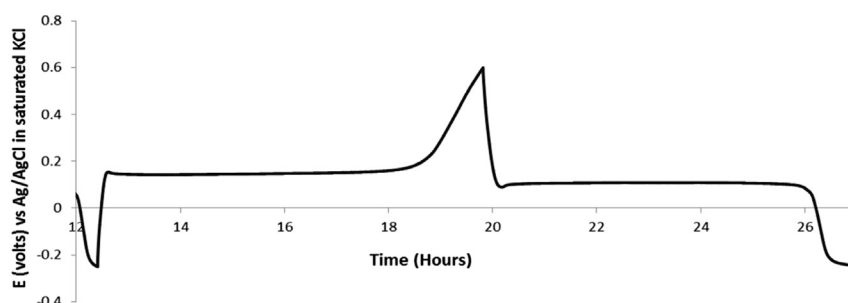


Fig. 4. Charge–discharge profile of $\text{K}_2\text{BaFe}(\text{CN})_6$ based positive electrodes for Ca^{2+} ion intercalation/de-intercalation with 1 M $\text{Ca}(\text{ClO}_4)_2$ in acetonitrile and 6 ml DI water.

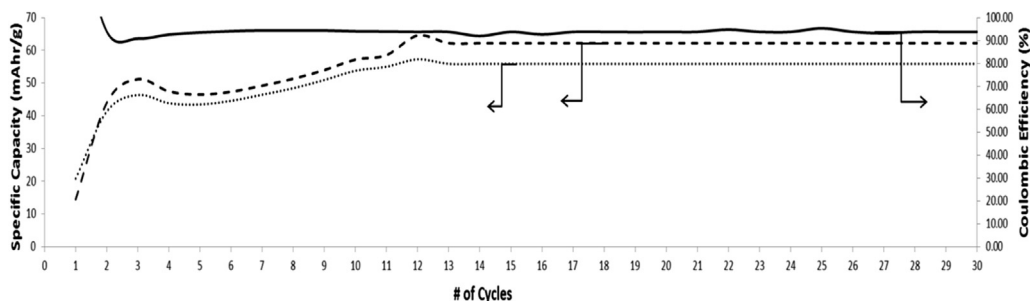


Fig. 5. Specific capacity (mA hr g^{-1}) vs. number of cycles and coulombic efficiency (%) for charge and discharge cycle. The charge capacity is represented by dashed line and the discharge capacity is represented by dotted line. The coulombic efficiency is represented by the solid line.

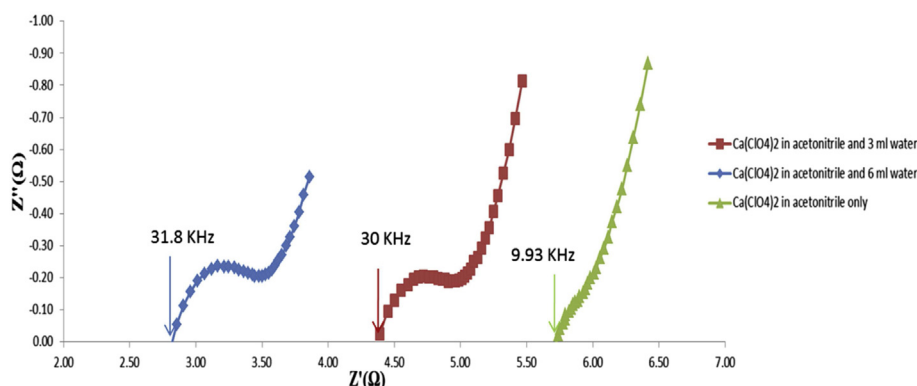


Fig. 6. Nyquist plots for $\text{K}_2\text{BaFe}(\text{CN})_6$ based electrode in 1 M calcium perchlorate ($\text{Ca}(\text{ClO}_4)_2$) in acetonitrile only, 1 M calcium perchlorate ($\text{Ca}(\text{ClO}_4)_2$) in acetonitrile and 3 ml water and 1 M calcium perchlorate ($\text{Ca}(\text{ClO}_4)_2$) in acetonitrile in 6 ml water.

4. Conclusion.

Development of multivalent rechargeable batteries will require investigation of electrode materials as well as electrolytes. As a step towards achieving this goal, we have examined $\text{K}_2\text{BaFe}(\text{CN})_6$, a Prussian blue analogue, for intercalation of divalent Ca^{2+} ions as a possible battery material. It is shown that addition of 17% water to the acetonitrile-based electrolyte leads to a significant increase in redox activity and the energy capacity of Ca^{2+} ions. The enhancement in the performance is attributed to the hydration effect. To date, the cathode has demonstrated a coulombic efficiency of around 93.8% with a reversible capacity of $55.8 \text{ mA hr g}^{-1}$. Currently, work is in progress to optimize this material system.

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